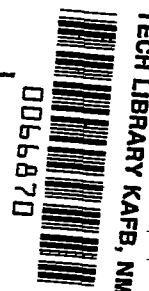# NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 4118

LOW-TEMPERATURE, VAPOR-PHASE OXIDATION OF

FUEL-RICH HYDROCARBON MIXTURES

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SUMMARY

The vapor-phase oxidation of methylcyclohexane was studied in a flow system in the temperature range of 300° to 400° C under the conditions of 0.1 the stoichiometric amount of oxygen, a contact time of 8 seconds, and a spiral Pyrex reactor 10.5 inches long with an inside diameter of 3/32 inch. The yields of acids, aldehydes, ketones, hydrogen peroxide, organic peroxides, olefin, water, and unreacted hydrocarbon were determined in the products.

It was found that, under these conditions, methylcyclohexane exhibits a negative temperature coefficient in its rate of oxidation at a temperature just above 310° C. The rate of reaction increased greatly between 300° and 310° C in a manner resembling the cool-flame type of reaction, although existing literature seems to indicate that cool flames should not occur in a reactor of these dimensions.

The yield of olefin, based on the amount of methylcyclohexane reacted, was found to reach a maximum in the range of the negative temperature coefficient and the yield of peroxides started at a high value and decreased with increasing temperature. The yields of other oxygenated materials, after a slight increase, steadily decreased with increasing temperature.

The above results can be fairly well interpreted on the basis of the concept of separate mechanisms for low-temperature and high-temperature oxidation. At low temperature, the hydroperoxide intermediates decompose to give chain branching

$$ROOH \longrightarrow RO\cdot + HO\cdot$$
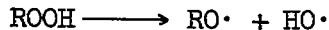
and at high temperature the peroxy radicals decompose before abstracting hydrogen in a reaction leading only to chain propagation

$$RCH_2OO\cdot \xrightarrow{\text{High temperature}} RCHO + HO\cdot$$
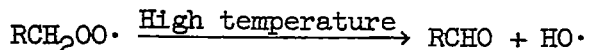
The evidence indicates that hydrocarbon-free-radical disproportionation may also contribute to the negative-temperature-coefficient phenomenon

$$2RCH_2CH_2 \cdot \longrightarrow RCH{=}CH_2 + RCH_2CH_3$$
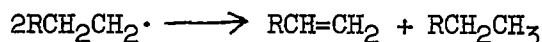
A small amount of aromatics was also noted in the products, and a dark-brown, tarry residue was formed at the exit end of the reactor in all the reactions. A small amount of this residue was obtained at 300° C where the extent of reaction was small and only olefin, organic peroxide, and carbonyl structures were detected in the products. It is therefore probable that these materials are precursors of tar and gum deposits.

It was attempted to study the reaction further by increasing the oxygen-fuel stoichiometry to 0.3 at 325° C with the same contact time. This reaction resulted in an explosion, which destroyed the two receivers and the Dewar flasks containing them.

INTRODUCTION

For propane and many higher paraffins there has been observed a range of temperature wherein, as the temperature is increased, the rate of oxidation of the hydrocarbon decreases (ref. 1). As the temperature is increased further, the rate passes through a minimum and then begins to increase again. This negative temperature coefficient, which has also been observed for some olefins, was first noted by Pease (ref. 2) in work on the oxidation of propane and butane. The range of the negative temperature coefficient is dependent on conditions such as pressure and stoichiometry and is sensitive to surface effects.

The explanations of the negative temperature coefficient which have been offered usually involve the theory that there are separate mechanisms for the low-temperature and the high-temperature oxidations of hydrocarbons. In the low-temperature mechanism it is thought that the peroxy radicals formed as intermediates abstract hydrogen to form hydroperoxides which decompose to give chain branching

$$R \cdot + O_2 \longrightarrow ROO \cdot \xrightarrow{\ RH\ } ROOH + R \cdot$$

$$ROOH \longrightarrow RO \cdot + HO \cdot$$
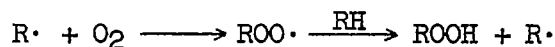
but as the temperature is increased, the peroxy radicals tend to decompose, before abstracting hydrogen, in a reaction which leads only to chain propagation

$$RCH_2OO \cdot \longrightarrow RCHO + HO \cdot$$
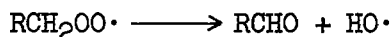
Thus the rate of oxidation could decrease with increasing temperature before the high-temperature mechanism, which probably involves more initial attacks by oxygen, had fully come into play.

Previous work performed in this laboratory (ref. 3) seemed to indicate that at 300° C methylcyclohexane might be nearing the range of temperature wherein it would exhibit a negative temperature coefficient for its rate of oxidation under the conditions studied and with the particular apparatus employed.

The present study had as objectives the determination of the range of the negative temperature coefficient for the oxidation of methylcyclohexane, the investigation of the distribution of some reaction products in this range in order to substantiate the proposed mechanisms, and the determination of the rate and mode of formation of high-molecular residues by oxidative coking.

This investigation was conducted at the University of Cincinnati under the sponsorship and with the financial support of the National Advisory Committee for Aeronautics.

DESCRIPTION OF APPARATUS AND PROCEDURE

The apparatus used for the oxidations is essentially the same as that employed in previous vapor-phase-oxidation work (ref. 3) conducted in this laboratory. Figure 1 is a schematic diagram of this apparatus. The temperature control was improved and a device for collecting the reaction gases was added.

The apparatus consists of: (1) A gas feeder, (2) a liquid-fuel feeder, (3) a fuel-and-gas mixer and preheater, (4) the reaction chamber, (5) condensing traps, and (6) the gas-collecting device. Tank oxygen was dried by passing it through a Drierite column. It was then passed through a flowmeter and led into the fuel-dropping adapter. The methylcyclohexane was conducted to this adapter by a constant-feed device (ref. 4). This feeder consisted of an 1,800-rpm Bodine electric motor, delivering a constant torque geared down from 250 to 1, a pair of circular gears (sometimes reducer gears were used in between), a vertical-drive screw with piston carriage, a steel piston, a precision-bore Pyrex glass cylinder, and a capillary lead to the dropping adapter. The motor turns the gears at a constant rate thus rotating the vertical screw at a constant rate. This raises the piston carriage and moves the piston through the stationary glass cylinder containing the liquid methylcyclohexane. The methylcyclohexane is forced through the capillary and through a small orifice in the adapter. A large variety of flow rates for the fuel can be obtained by varying the gear ratio or the cylinder diameter or both. A pointer

attached to the piston carriage and moving along an adjacent linear
millimeter scale measures the amount of fuel delivered. The cylinder
used in this work was a Pyrex tube with a 3/8-inch inside diameter, for
which the maximum deviation from the average feed rate was 0.4 percent.
A Hycar O-ring was fitted to the head of the piston to insure uniform
flow without leakage. This O-ring was lubricated with glycerine previous
to runs to avoid sticking in the cylinder.

The fuel droplets in the adapter were vaporized and mixed with the
incoming oxygen by passing them through an 8-inch length of Pyrex tubing
packed with glass helices and encased in the preheater furnace. The
glass helices assured better mixing of the oxygen and hydrocarbon vapor
and also minimized any tendency for reaction in the preheater by pro-
viding high surface effects. The fuel-oxygen mixture of known composi-
tion was then passed through the spiral Pyrex reaction tube (3/32-inch
inside diameter and 10.5 inches long) at a given temperature and contact
time. The temperature of the preheater coil was controlled with a
variable transformer.

For controlling the temperature of the reaction chamber a commercial
unit called an Amplitrol was used. The power source is connected to the
Amplitrol and power flows from the Amplitrol through a variable trans-
former to the Nichrome wire of the reactor furnace. A Chromel-Alumel
thermocouple is positioned as indicated in figure 1, and its leads are
connected to the Amplitrol. The variable transformer is set at a reading
slightly higher than that which would give the desired temperature without
the Amplitrol, and then the dial of the Amplitrol is set at the desired
reading on the scale which is calibrated in $^\circ$C. The Amplitrol automati-
cally turns the power on or off according to the voltage of the thermo-
couple and consequently according to the temperature of the reactor.
When equilibrium is reached, the power is alternately turned on and off
every few seconds. The accuracy of the dial settings and the constancy
of the temperature obtained were checked with a calibrated potentiometer
and both were found to be very good. Figure 2 shows the temperature
distribution inside the reactor furnace.

After the gas mixture passed through the reaction tube, the reaction
was quickly quenched and the products condensed in two receivers, the
first immersed in an ice-water bath and the second, in a mixture of carbon
tetrachloride, chloroform, and dry ice at -70° C.

In later work the reaction gases and unreacted oxygen were collected
by connecting a piece of tubing from the second receiver through a three-
way stopcock to a large separatory funnel filled with water. At the
bottom of the funnel was attached a piece of glass tubing drawn to a
small opening so that no water flowed from the funnel unless gas was
admitted at the top. One outlet of the three-way stopcock was open to
the room, and the gas was allowed to flow out of this opening until the

reaction was started. The stopcock was then turned so that the gases were directed into the separatory funnel where they displaced the water. The volume of gas collected was determined by the volume of water displaced, corrections being made for the vapor pressure of water and for atmospheric pressure.

A series of oxidation reactions was carried out with methylcyclohexane between 300° and 400° C. The contact time was 8 seconds in all experiments and one-tenth of the stoichiometric amount (for complete reaction to carbon dioxide and water) was used; thus the reaction mixtures were composed of 1.05 moles of oxygen per mole of methylcyclohexane. The extent of reaction at the constant contact time was taken as a measure of the relative rates of oxidation at the various temperatures.

The condensates were divided into a water phase and an organic phase, and the organic phase was extracted with water several times. These washings were combined with the original water phase and diluted to 25 milliliters. Analyses were then made for unreacted hydrocarbon, olefin, and aromatic compounds by chromatography using fluorescent adsorption indicators (ref. 5) as follows: An aliquot of the organic phase was mixed with a small amount of fluorescent indicator dye and placed on a 4-foot-long Pyrex column having a 1/16-inch inside diameter and filled with anhydrous silica gel (fig. 3). The sample was then forced down the column under 3 to 8 pounds per square inch of nitrogen using ethanol as the eluate. The constituents move down the column at a rate dependent on their polarity, the oxygenated compounds being absorbed most strongly and the saturates being absorbed least strongly. Each band is identifiable under ultraviolet light; the aromatics fluoresce violet; the olefins, yellow; and the saturates, not at all. The olefin and saturates were collected in a cooled iodine flask, the cut being made at the appearance of the first drop of violet. The weight of the olefin in this sample was determined by the bromate-bromate method (ref. 6) assuming that the olefin was methylcyclohexane. To the weighed sample of saturates and olefins in a titration flask was added approximately 20 percent excess of standard 0.2N bromate-bromide solution, 5 milliliters of 6N H_2SO_4, 15 milliliters of 0.2N $HgSO_4$ catalyst solution, and 15 milliliters of glacial acetic acid. After shaking the solution in the dark for about 7 minutes, 15 milliliters of 2N NaCl were added (to release the bromine adsorbed on the catalyst) followed by 15 milliliters of 20 percent KI solution. The liberated iodine was titrated with standard 0.1N $Na_2S_2O_3$ solution. This titration indicated the quantity of excess bromate-bromide solution; hence the weight of olefin in the sample could be calculated. The weight of unreacted methylcyclohexane in the sample was found by difference.

Total peroxides were determined iodometrically. A piece of dry ice was added to 10 milliliters of glacial acetic acid in a titration flask

to sweep out the air. To this was added the sample and, after excess potassium iodide solution was added, it was allowed to stand in the dark for half an hour. The liberated iodine was titrated with 0.1N $Na_2S_2O_3$ solution. This procedure was followed with both phases.

Hydrogen peroxide was determined colorimetrically by the reaction with titanium sulfate reagent (ref. 6). An aliquot of the water phase was diluted to volume with the reagent and the percent light absorption at 420 millimicrons was measured with a spectrophotometer. The value of the hydrogen peroxide content corresponding to this percent absorption was read directly from a graph obtained previously from known solutions of hydrogen peroxide.

Carbonyl compounds were determined gravimetrically by precipitation of the 2,4-dinitrophenylhydrazones using the reagent solution described by Shriner and Fuson (ref. 7).

Aldehydes were determined gravimetrically by precipitation of the methone derivatives as described by Walker (ref. 8) and acids were determined by simple titration with standard 0.1N base using phenolphthalein as indicator.

The reaction gases were analyzed for carbon dioxide, oxygen, carbon monoxide, and total gaseous olefin with a Burell Industro Gas Analyzer (model C).

RESULTS AND DISCUSSION

A series of preliminary oxidation runs were made on methylcyclohexane before the Amplitrol was received and installed in the apparatus. In these runs the temperature was controlled by a variable transformer. Although difficulty was encountered in trying to maintain a constant temperature, the results given in table I seemed to indicate that the negative temperature coefficient for methylcyclohexane was between 300° and 400° C. Therefore, after the Amplitrol was installed and the oxygen flowmeter recalibrated, a second series of runs was made in this range and the change in distribution of products with temperature was examined.

Table II(a) and figure 4 show that with the improved temperature control there was very little reaction at 300° C. However, on increasing the imposed temperature by only 10° to 310° C, the amount of reaction occurring at the same contact time was increased tremendously. Further increase of the temperature, however, at first decreased the amount of reaction and then gradually increased it. Thus, under the conditions employed, methylcyclohexane exhibits its negative temperature coefficient for oxidation at slightly over 310° C.

The large increase in the amount of reaction between 300° and 310° C resembles the cool-flame type of phenomenon, wherein, under a given set of conditions with a given hydrocarbon, there is a temperature below which the cool flame cannot be obtained. Although the room was darkened during the course of some of the runs, no luminosity could be observed. However, the amount of reaction and the type of products are similar to those obtained by Oberdorfer (ref. 9) in his work on cool flames. Spence and Townend (ref. 10) state that no cool flames could form in a reaction tube less than 6 millimeters in diameter, whereas the present reactor is only about $2\frac{1}{2}$ millimeters in diameter. Williams, Johnson, and Carhart (ref. 11) have recently provided evidence that a cool-flame reaction may continue in a small-diameter tube if already started in a larger one.

It is fairly well established (refs. 12 to 14) that the luminosity of the cool flame comes from excited formaldehyde molecules. Possibly in a small-diameter tube the amount of formaldehyde in a given cross section of the tube is not sufficient for luminosity to be observed.

It is realized, of course, that the actual temperature inside the reactor may have increased appreciably beyond the imposed temperature of 310° C measured on the outside of the reactor. The inability to measure inside temperatures is a real limitation of the present apparatus. Were such measurements possible, the evidence for cool flames would have been decisive.

Table II(a) reports the yields of the products based on the amount of methylcyclohexane reacted, whereas table II(b) reports the yields based on the amount of methylcyclohexane passed through the reactor. The yields are plotted against temperature in both ways in figures 5 through 10. The first type of plot is an indication of the fate of the methylcyclohexane which has actually reacted whereas the latter simply shows what has happened to the methylcyclohexane passed through the reactor at the different temperatures.

From tables II(a) and II(b) and figure 5 it can be seen that the yield of olefin, based on the amount of methylcyclohexane reacted, at first increases on increasing the temperature from 310° C, reaches a maximum, and begins to decrease. The yield of olefin, based on the amount of methylcyclohexane passed, increases steeply at first and then levels off to a very gradual increase. Robertson (ref. 1) has observed that, at high hydrocarbon-to-oxygen ratios for propane, butane, and isobutane, the maximum production (based on hydrocarbon reacted) of propylene, butylene, and isobutylene, respectively, corresponds to the minimum rate.

Table II(a) and figure 6 show that the yields of hydrogen peroxide and organic peroxide, based on the methylcyclohexane reacted, start at high values at 310° C and decrease with increasing temperature. The

yield of organic peroxide above a given temperature decreases much faster
than that of the hydrogen peroxide, which at the higher temperature is
decreasing very little. At 310° C there is more organic peroxide than
hydrogen peroxide, whereas at 375° C the reverse is true. The yields,
based on the amount of methylcyclohexane passed (table II(b), fig. 7),
of course start at low values of 300° C where the amount of reaction
was low, increase rapidly on increasing the temperature to 310° C, and
thereafter resemble the former plots in shape.

Figure 8 shows that the yields of acid, aldehyde, and ketone, based
on the amount of methylcyclohexane reacted, at first increase on increasing
the temperature from 310° C, reach a maximum on further increase in
temperature, and then begin to decrease steadily. The yield of acid is
about 10 times that of the aldehyde. The ratio of ketone to aldehyde
starts at about 2 at 310° C, decreases to a minimum on increasing the
temperature, and then increases back to approximately 2 at 375° C. In
figure 9 the yields of acid, aldehyde, and ketone, based on the amount
of methylcyclohexane passed, give plots of shape similar to those in
figure 8. However, the yields calculated in this way have about half the
value of those calculated in the former way.

From figure 10 it can be seen that the yield of water, based on the
amount of hydrocarbon reacted, decreases rather gradually on increasing
the temperature from 310° C. The yield, based on the amount of methyl-
cyclohexane passed, increases very fast from 300° to 310° C, decreases
slightly to a minimum on further increase in temperature, and then
increases slightly again. This minimum production of water seems to
correspond to the minimum amount of reaction. It is interesting to note
that in all the cases of extensive reaction the water accounts for a
large majority of the oxygen passed through the reactor.

In all the oxidation runs made on methylcyclohexane in this investi-
gation there was obtained a small amount of dark-brown, tarry residue at
the exit end of the reaction tube. Even at 300° C where the amount of
reaction was small some of this residue was obtained. At 310° C the
quantity of residue increased sharply but above this temperature the
amount of residue did not seem to vary greatly with the temperature.
At the higher temperatures, however, it was harder and more cokelike.

There was also observed a small amount of aromatic material when
the organic phases from the reactions were chromatographed. The amount
of these aromatics varied between about 1 and 2 volume percent of the
organic phases.

Runs 7 and 8 were both done at 325° C as a means of checking the
reproducibility of the results. Tables II(a) and II(b) show that there
was fairly good reproducibility in the extent of reaction, and there was
fair agreement in the yield of products.

In table III are reported the analyses of the reaction gases from one of the reactions at 325° C and the reaction at 375° C. As can be seen from the table, most of the oxygen was consumed; however, there was a measurable increase in the amount of oxygen consumed between 325° and 375° C as well as an increase in the amount of reaction (table I). It is therefore likely that it was not the complete consumption of oxygen which was responsible for the negative temperature coefficient observed. The yield of carbon dioxide decreased with the increase in temperature and the yield of carbon monoxide increased.

A sample of the reaction gases from the reaction at 375° C was analyzed by mass spectrometry and was shown to contain hydrogen, methane, ethane, ethylene, propane, propylene, butane, and butylenes, as well as oxygen, carbon dioxide, and carbon monoxide. The yields of these additional products, based on the amount of methylcyclohexane reacted, were:

Product	Moles product per mole methylcyclohexane reacted
Hydrogen	0.043
Methane	.021
Ethane	.005
Ethylene	.075
Propane	.005
Propylene	.030
Butane	.005
Butylenes	.007

Ethylene is the hydrocarbon present in largest amount and the olefins, in general, make up the bulk of the hydrocarbons present. These products probably result from the oxidation since the temperatures are not high enough for pyrolysis.

The results of oxygen balances for runs at 325° and 375° C are given in table IV. In each case 98 percent of the oxygen was accounted for. Table V shows that the mass balances for these runs were 95 and 94 percent, respectively. With these results it was felt that it was reasonable to attempt an interpretation of the results obtained, writing plausible reactions to account for products. Owing to the complexity of the problems encountered in hydrocarbon oxidation, the discussion is necessarily highly speculative and is not intended to be conclusive.
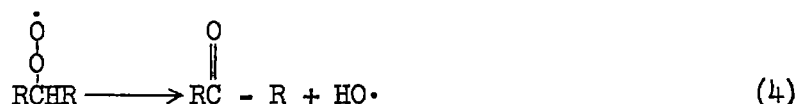
If one of the factors contributing to the negative temperature coefficient is decomposition of peroxy radicals

$$RCH_2OO\cdot \longrightarrow RCHO + HO\cdot \tag{1}$$
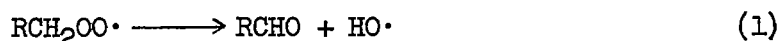
to give chain propagation before the radicals can abstract hydrogen to form the hydroperoxides, which react to give chain branching

$$ROO\cdot + RH \longrightarrow R\cdot + ROOH \tag{2}$$

$$ROOH \longrightarrow RO\cdot + HO\cdot \tag{3}$$

then one would expect to find organic peroxides present in largest amount at the temperature just below that of the negative temperature coefficient. Examination of figures 6 and 7 shows that this is the case. A primary peroxy radical would decompose as in equation (1) to give an aldehyde, and a secondary peroxy radical would decompose to give a ketone as follows:

$$\overset{\overset{\displaystyle \cdot}{\underset{\displaystyle O}{\overset{\displaystyle O}{|}}}}{RCHR} \longrightarrow \overset{\overset{\displaystyle O}{\|}}{RC} - R + HO\cdot \tag{4}$$

Figures 8 and 9 show that the yields of these products increase in the range of the negative temperature coefficient. The fact that the yield of hydrogen peroxide does not decrease as fast as that of the organic peroxides with increasing temperature might be attributed to the increasing free-radical character of oxygen with increasing temperature shown as follows:

$$RH + O_2 \xrightarrow{\text{High temperature}} R\cdot + HO_2\cdot \tag{5}$$

$$HO_2 + RH \longrightarrow R\cdot + H_2O_2 \tag{6}$$
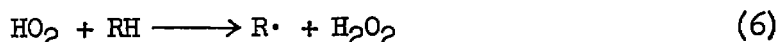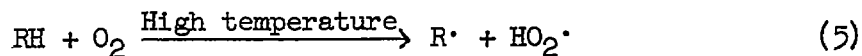
Another reaction which could help account for the negative temperature coefficient is an increasing rate of disproportionation of hydrocarbon free radicals with increasing temperature shown by

$$2RCH_2CH_2\cdot \longrightarrow RCH=CH_2 + RCH_2CH_3 \tag{7}$$
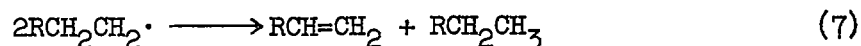
This reaction not only would remove two chain carriers to slow the rate but would also serve to regenerate a molecule of the original hydrocarbon, which would cause the apparent rate to be less. This would also be in line with the increase in the yield of olefin in the range of the negative temperature coefficient. A hydrocarbon radical could also decompose into an olefin and atomic hydrogen (eq. 8), which could abstract a hydrogen (eq. 9) to account for the hydrogen present in the reaction gases from the reaction at 375° C. These equations are

$$RCH_2CH_2 \cdot \longrightarrow RCH=CH_2 + H \cdot \tag{8}$$

$$H \cdot + RH \longrightarrow R \cdot + H_2 \tag{9}$$
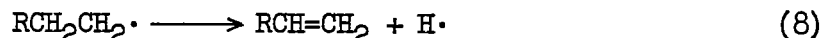
The high yield of water is evidence that the initial products and subsequent products of the oxidation of methylcyclohexane react at a faster rate than does the methylcyclohexane. This is entirely plausible because ring compounds are relatively stable to oxidation, as is the methyl group, and reaction of a molecule of methylcyclohexane will lead to rupture of the ring to produce straight chain molecules with methylene groups, which are very susceptible to oxidation. Initial attacks on methylcyclohexane would probably be principally at secondary carbons because of their number and because the one tertiary carbon is somewhat shielded, which can be shown as follows:
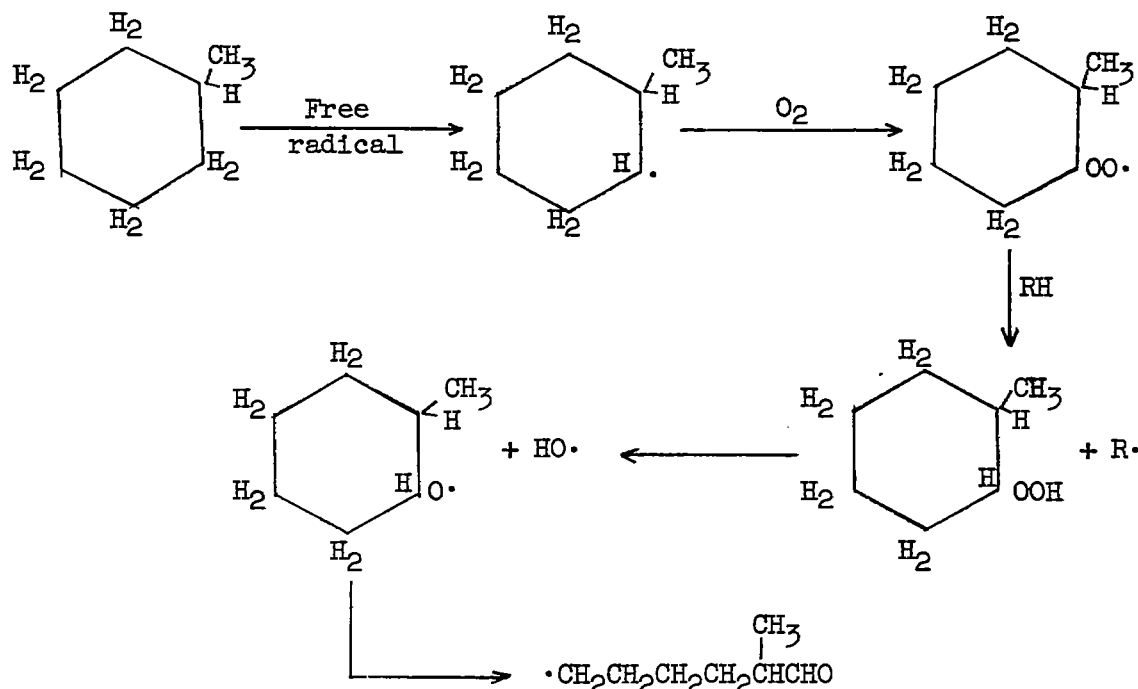
From the above scheme it can be seen that attack on methylcyclohexane leads to products which are more susceptible to oxidation than is the methylcyclohexane. The acid found in the products could arise from further oxidation of aldehydes. The water would, of course, arise from abstraction of hydrogen by hydroxyl free radicals.

Lewis and Von Elbe (ref. 15) state that the preferred position of attack is the CH=O group and that the resulting radical RCO· decomposes into R· and CO·. This could give rise to the carbon monoxide. The carbon dioxide could arise from further oxidation of the carbon monoxide.

The hydrocarbons in the gaseous products probably result from decomposition of large intermediate hydrocarbon free radicals as

$$RCH_2CH_2· \longrightarrow R· + CH_2=CH_2$$
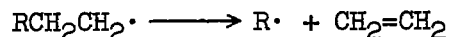
Rice and Rice (ref. 16) state that large hydrocarbon free radicals easily decompose into more stable, smaller free radicals.

Some of the dark-brown, tarry residue obtained in the reactions was extracted with carbon tetrachloride and carbon disulfide; the material was only very slightly soluble in these solvents. An infrared spectrum was obtained on these extracts but was not revealing except for a slight peak which probably corresponds to carbonyl groups.

A carbon and hydrogen analysis was also obtained on a sample of this residue with the following results:

Carbon, percent 64.73
Hydrogen, percent 6.89
Oxygen (by difference), percent 28.4

These values correspond to atomic ratios of 0.78 and 3.4 for carbon to hydrogen and for carbon to oxygen, respectively. The low ratio of carbon to hydrogen precludes the possibility that the residue contains much aromatic material. With the evidence at hand, however, very little can be said about the actual nature of this residue. The fact that some of this residue was obtained at 300° C where no hydrogen peroxide, acid, or water was detected in the products seems to indicate that at least these materials probably are not involved in its formation. These residues somewhat resemble gum deposits for which, as yet, no adequate explanation has been formulated (ref. 17) although olefins and organic peroxides are recognized as contributing to its formation.

CONCLUSIONS

From the investigation of the vapor-phase oxidation of methylcyclo-hexane with fuel-rich mixtures the following conclusions can be drawn:

1. Under the conditions of 0.1 the stoichiometric amount of oxygen and a contact time of 8 seconds in a spiral reactor 10.5 inches long with an inside diameter of 3/32 inch, methylcyclohexane exhibits a negative temperature coefficient for its rate of oxidation at just above 310° C.

2. The extent of reaction at 310° C and the products secured are similar to those obtained in work on cool flames.

3. The yield of olefins, based on the amount of methylcyclohexane reacted, reaches a maximum in the range of the negative temperature coefficient.

4. The yield of peroxides decreases on increasing the temperature in this range; hydrogen peroxide does not increase so much as the organic peroxides.

5. The yields of other oxygenated materials, after a slight increase, steadily decrease on increasing the temperature.

6. Dark-brown, tarry residues are obtained at the exit end of the reactor in these reactions. These deposits do not appear to be caused by dehydrogenation (oxidation) of intermediate products but seem to arise by condensation reactions of aldehydes and ketones.

7. The evidence seems to support the peroxy-radical decomposition as a factor in the negative-temperature-coefficient range with the possibility that hydrocarbon-radical disproportionation is also a factor.

University of Cincinnati,
    Cincinnati, Ohio, July 30, 1956.

REFERENCES

1. Robertson, N. C.: The Chemistry of Petroleum Hydrocarbons. Reinhold
   Pub. Corp., Ch. 36, 1955, pp. 365-397.

2. Pease, R. N.: Characteristics of the Non-Explosive Oxidation of Pro-
   pane and the Butanes. Jour. Am. Chem. Soc., vol. 51, no. 6, June
   1929, pp. 1839-1856.

3. Swarts, Donald: Oxidative Degradation of Methylcyclohexane and
   n-Heptane. Contract NAw-6401, NACA and Univ. of Cincinnati,
   Aug. 10, 1955.

4. Jones, B. W., Jones, S. A., and Neuworth, M. B.: Precision Liquid
   Feeder. Ind. and Eng. Chem., vol. 44, no. 9, Sept. 1952,
   pp. 2233-2234.

5. Criddle, Dean W., and Le Tourneau, Robert L.: Fluorescent Indicator
   Adsorption Method for Hydrocarbon-Type Analysis. Analytical Chem.,
   vol. 23, no. 11, Nov. 1951, pp. 1620-1624.

6. Eisenberg, George M.: Colorimeter Determination of Hydrogen Peroxide.
   Ind. and Eng. Chem., vol. 15, no. 5, May 18, 1943, pp. 327-328.

7. Shriner, Ralph L., and Fuson, Reynold C.: The Systematic Identifica-
   tion of Organic Compounds. John Wiley & Sons, Inc., 1948, pp. 97-98.

8. Walker, J. F.: Formaldehyde. Am. Chem. Soc. Monograph Ser. No. 98,
   1944, pp. 264-266.

9. Oberdorfer, Paul E.: The Cool-Flame Combustion of the Isomeric
   Hexanes. Thesis, Ohio State Univ., 1954.

10. Spence, Kate, and Townend, D. T. A.: The Two-Stage Process in the
    Combustion of Higher Hydrocarbons and Their Derivatives. Third
    Symposium on Combustion, Flame and Explosion Phenomena, Williams &
    Wilkins Co. (Baltimore), 1949, pp. 404-414; discussion, pp. 414-415.

11. Williams, H. G., Johnson, J. E., and Carhart, H. W.: Sampling Studies
    of Cool Flames. Ind. and Eng. Chem., vol. 47, no. 12, Dec. 1955,
    p. 2528.

12. Emelius, H. J.: The Spectra of the Phosphorescent Flames of Carbon
    Disulphide and Ether. Jour. Chem. Soc., 1926, pp. 2948-2951.

13. Emelius. H. J.: The Light Emission From the Phosphorescent Flames of
    Ether, Acetaldehyde, Propionaldehyde and Hexane. Jour. Chem. Soc.,
    1929, pp. 1733-1739.

14. Gaydon, A. G.: Spectroscopy and Combustion Theory. Chapman & Hall, Ltd. (London), 1948.

15. Lewis, Bernard, and Von Elbe, Guenther: The Chemistry of Petroleum Hydrocarbons. Reinhold Pub. Corp., ch. 32, 1955, pp. 277-308.

16. Rice, F. O., and Rice, K. K.: The Aliphatic Free Radicals. The Johns Hopkins Press (Baltimore), 1935.

17. Rosenwald, R. H.: ·The Chemistry of Petroleum Hydrocarbons. Reinhold Pub. Corp., ch. 34, 1955, pp. 325-355.

TABLE I

PRELIMINARY OXIDATION OF METHYLCYCLOHEXANE

(WITHOUT AMPLITROL)

[Conditions: Fraction of stoichiometry, 0.1;
contact time, 8 seconds]

Run	Temperature, °C	Percent reaction
1	300	53
2	325	47
3	350	46
4	375	47
5	400	57

TABLE II

OXIDATION OF METHYLCYCLOHEXANE

(a) Based on amount of methylcyclohexane reacted

Reaction number	6	12	7	8	9	11
Conditions:						
Fraction of stoichiometry	0.1	0.1	0.1	0.1	0.1	0.1
Temperature, °C	300	310	325	325	350	375
Contact time, sec	8.0	8.0	8.0	8.0	8.0	8.0
Analysis:						
Methylcyclohexane reacted, percent . . .	3.9	49	46	47	49	54
[a]Olefin, percent	0.17	0.09	0.17	0.17	0.18	0.16
[b]Hydrogen peroxide, percent	None	38	26	24	15	12
[b]Organic peroxide, percent	11	40	35	40	15	23
[b]Aldehyde (taken as CH_2O), percent . . .	12	6.6	19	16	14	9.0
[b]Ketone (taken as acetone), percent . . .	24	14	27	22	21	17
[a]Water, percent	None	3.4	3.0	3.1	3.0	2.8
[b]Acid, percent	None	178	185	183	118	73

[a]Moles product per mole methylcyclohexane reacted.

[b]Millimoles product per mole methylcyclohexane reacted.

TABLE II.- Concluded

OXIDATION OF METHYLCYCLOHEXANE

(b) Based on amount of methylcyclohexane passed through reactor

Reaction number	6	12	7	8	9	11
Conditions:						
Fraction of stoichiometry	0.1	0.1	0.1	0.1	0.1	0.1
Temperature, $^{\circ}$C	300	310	325	325	350	375
Contact time, sec	8.0	8.0	8.0	8.0	8.0	8.0
Analysis:						
[a]Olefin, percent	0.0067	0.044	0.076	0.081	0.081	0.088
[b]Hydrogen peroxide, percent	None	19	12	11	7.5	6.3
[b]Organic peroxide, percent	0.42	20	16	19	7.4	1.2
[b]Aldehyde (taken as HCH=O), percent . . .	0.47	3.2	8.6	7.4	6.7	4.8
[b]Ketone (taken as acetone), percent . . .	0.93	7.1	12	10	10	9.2
[a]Water, percent	None	1.7	1.4	1.4	1.4	1.5
[a]Acid, percent	None	88	84	86	57	39

[a]Moles product per mole methylcyclohexane passed.

[b]Millimoles product per mole methylcyclohexane passed.

TABLE III

ANALYSIS OF REACTION GASES

	Run 10	Run 11
Temperature, ^{o}C	325	375
Carbon dioxide, moles	0.0076	0.0043
Carbon monoxide, moles	0.019	0.042
Oxygen collected, ml	188	80
Carbon dioxide per mole hydrocarbon reacted, moles	0.13	0.064
Carbon monoxide per mole hydrocarbon reacted, moles	0.34	0.61
Oxygen passed, ml	2908	3260
Oxygen unreacted, percent	6.5	2.5

TABLE IV

OXYGEN BALANCE

	Run 10	Run 11
Temperature, ^{o}C	325	375
Volume collected as oxygen, ml	188	80
Volume collected as carbon dioxide, ml	188	108
Volume collected as carbon monoxide, ml	235	524
Volume collected as acid, ml	209	120
Volume collected as peroxide, ml	104	24
Volume collected as carbonyl, ml	16	22
Volume collected as water, ml	1920	2330
Total volume collected, ml	2860	3090
Oxygen accounted for, percent	98	98

TABLE V

MASS BALANCE

	Run 10	Run 11
Temperature, °C	325	375
Weight of condensate, g	13.99	14.34
Weight of oxygen in water, g	2.50	3.40
Weight of oxygen in other products, g	0.08	0.06
Net weight of carbon and hydrogen in condensate, g	11.41	10.88
Weight of carbon and hydrogen in gases, g	0.234	0.62
Total weight of carbon and hydrogen, g	11.6	11.5
Weight of hydrocarbon passed, g	12.2	12.2
Percent accounted for of weight passed	95	94

A - Regulator gage
B - Drying tubes
C - Flowmeter
D - Gas mixing bottle
E - Constant-speed motor
F - Gears
G - Pointer, on screw
H - Scale, mm
I - Screw
J - Ball bearings
K - Steel piston
L - Hycar o-ring
M - Precision bore cylinder
N - Liquid fuel
O - Capillary lead
P - Fuel-dropping adapter
Q - Thermocouple
R - Preheating furnace, 8"
S - Powered iron conductor
T - Preheating coil
U - Combustion furnace, 13"
V - St. steel reactor housing (1 1/4" X 14")
W - Reactor tube, quartz (1/16"ID X 14")
X - 3-way stopcock
Y - Primary condensing receiver
Z - Secondary condensing receiver
AA- Bubbler
BB - Exit gas trap
CC - Dewar flask (-70° C)
DD - CuO Oxidizing furnace (for CO)
EE - Anhydrone tube
FF - Ascarite tube (for CO_2)

Figure 1.- Apparatus for oxidative-coking studies.
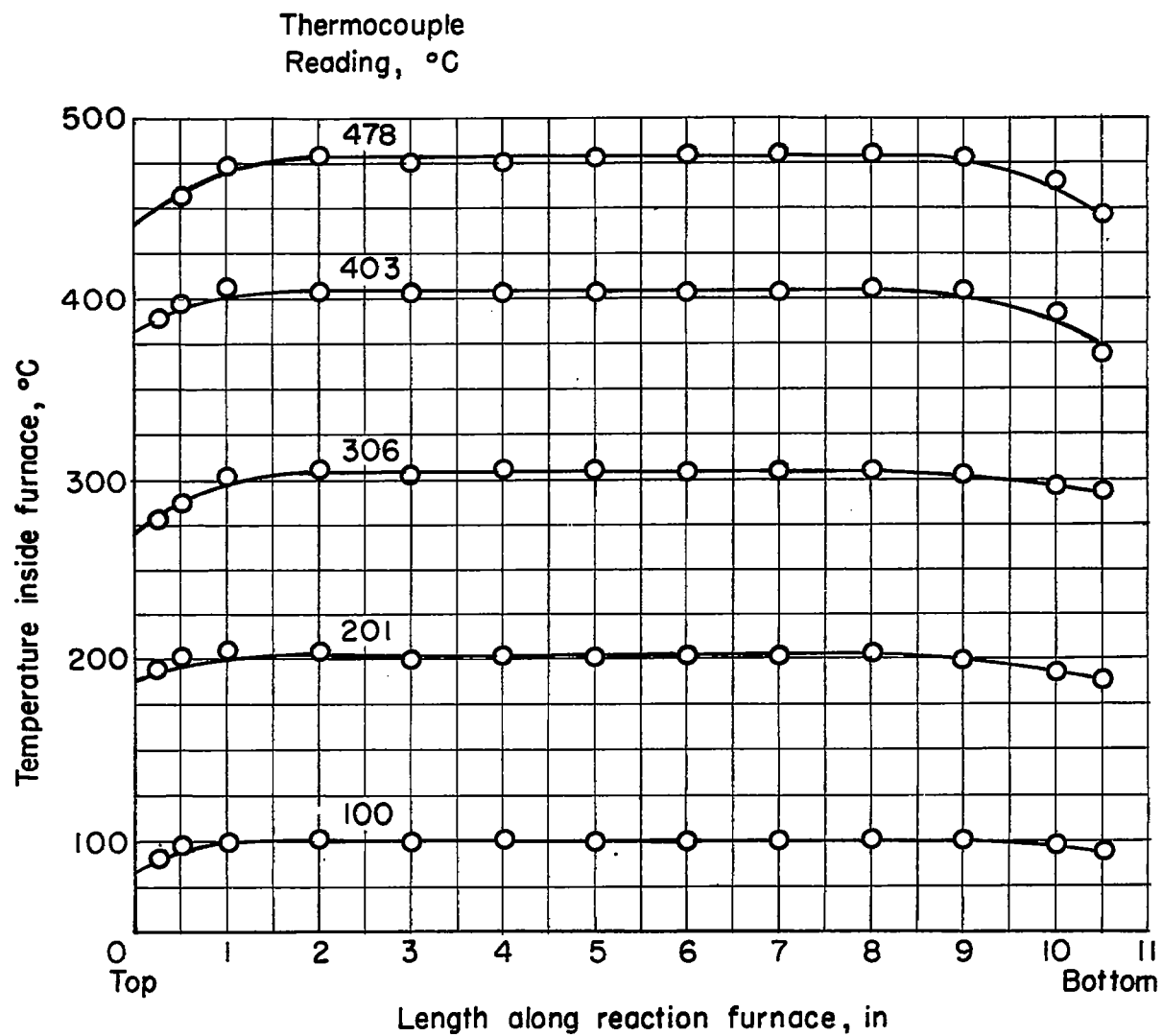
Figure 2.- Temperature distribution in reaction furnace.
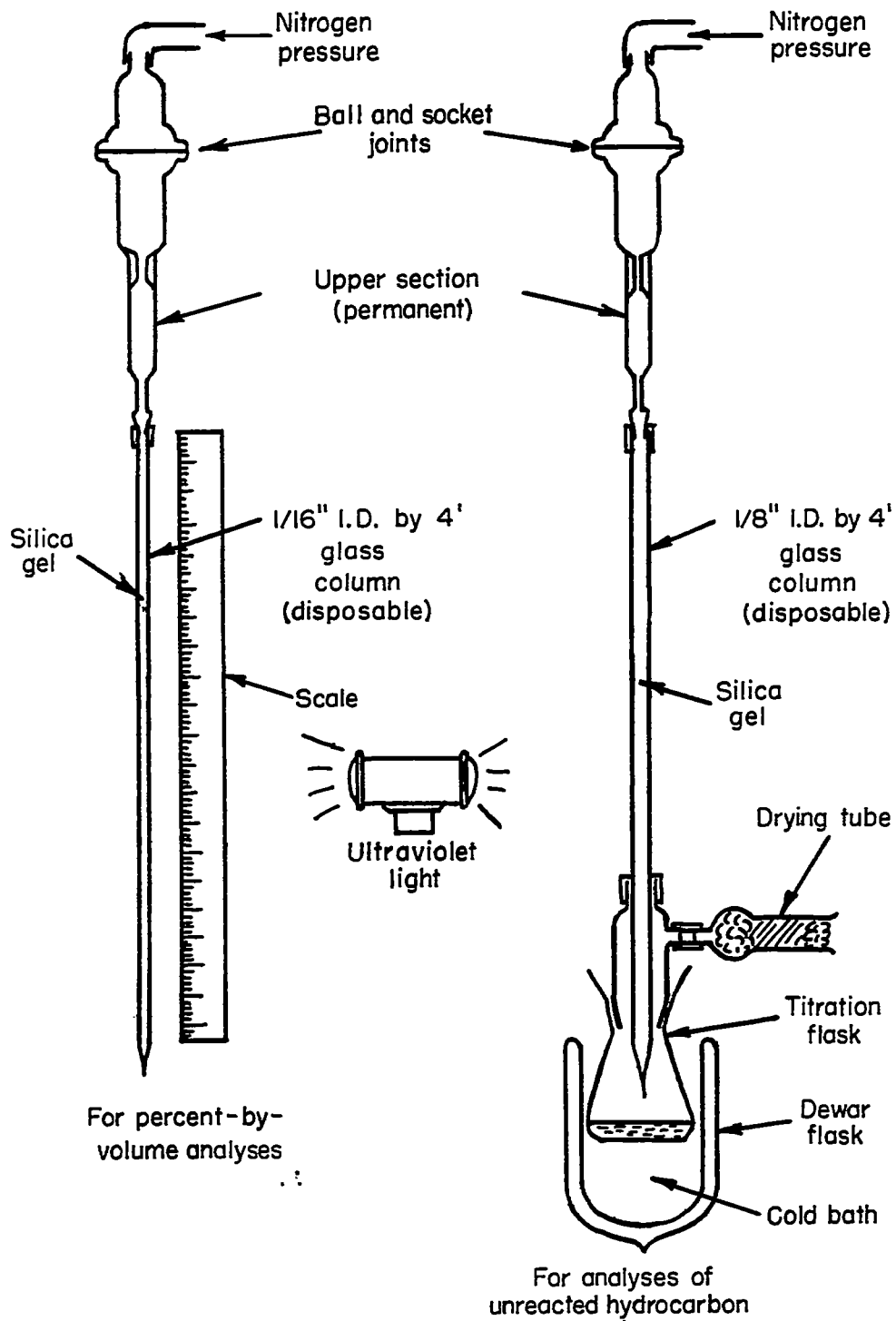
Figure 3.- Apparatus for chromatographic analyses.
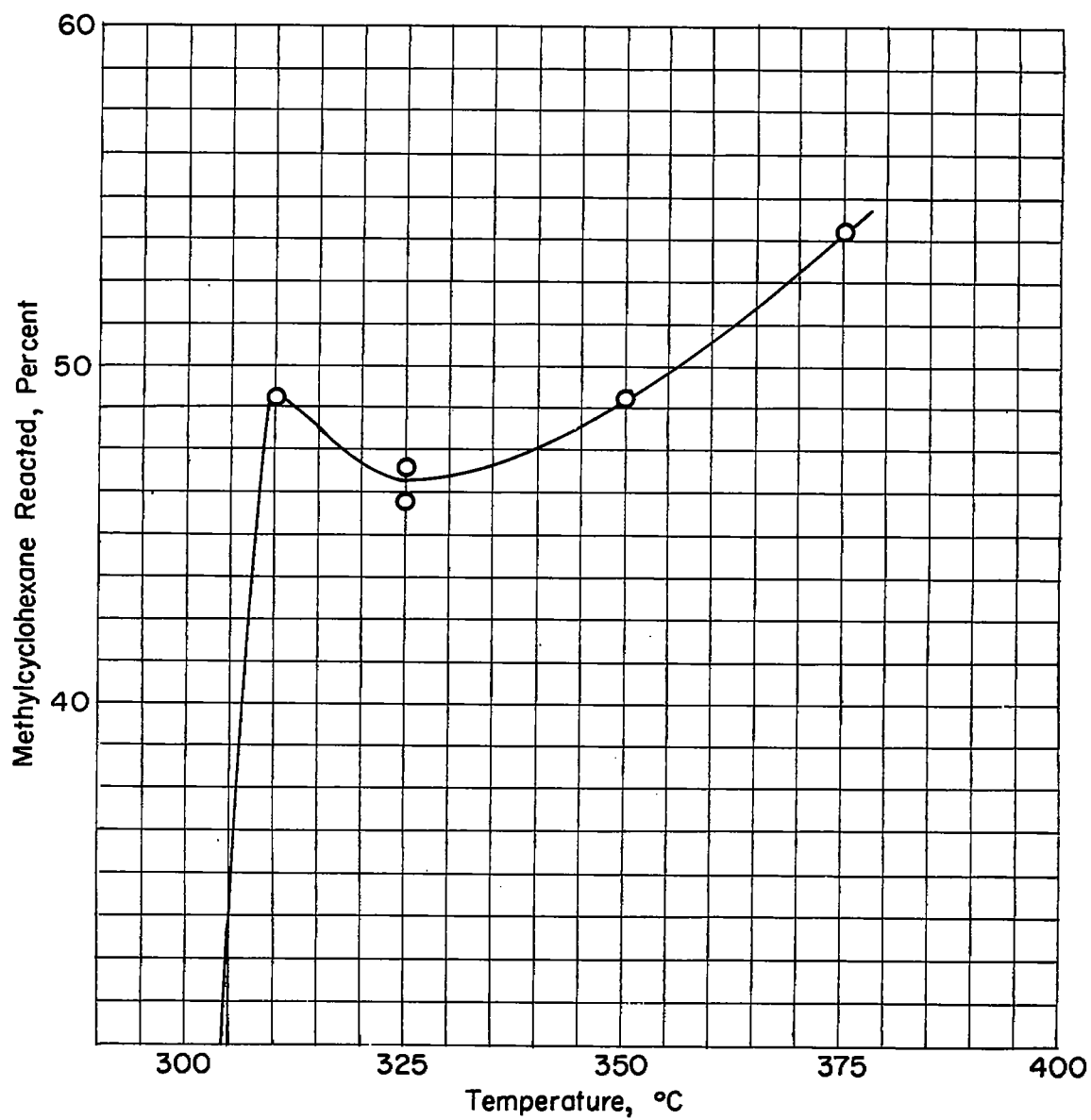
Figure 4.- Comparison of amount of reaction at various temperatures. Contact time, 8 seconds; stoichiometry, 0.1.
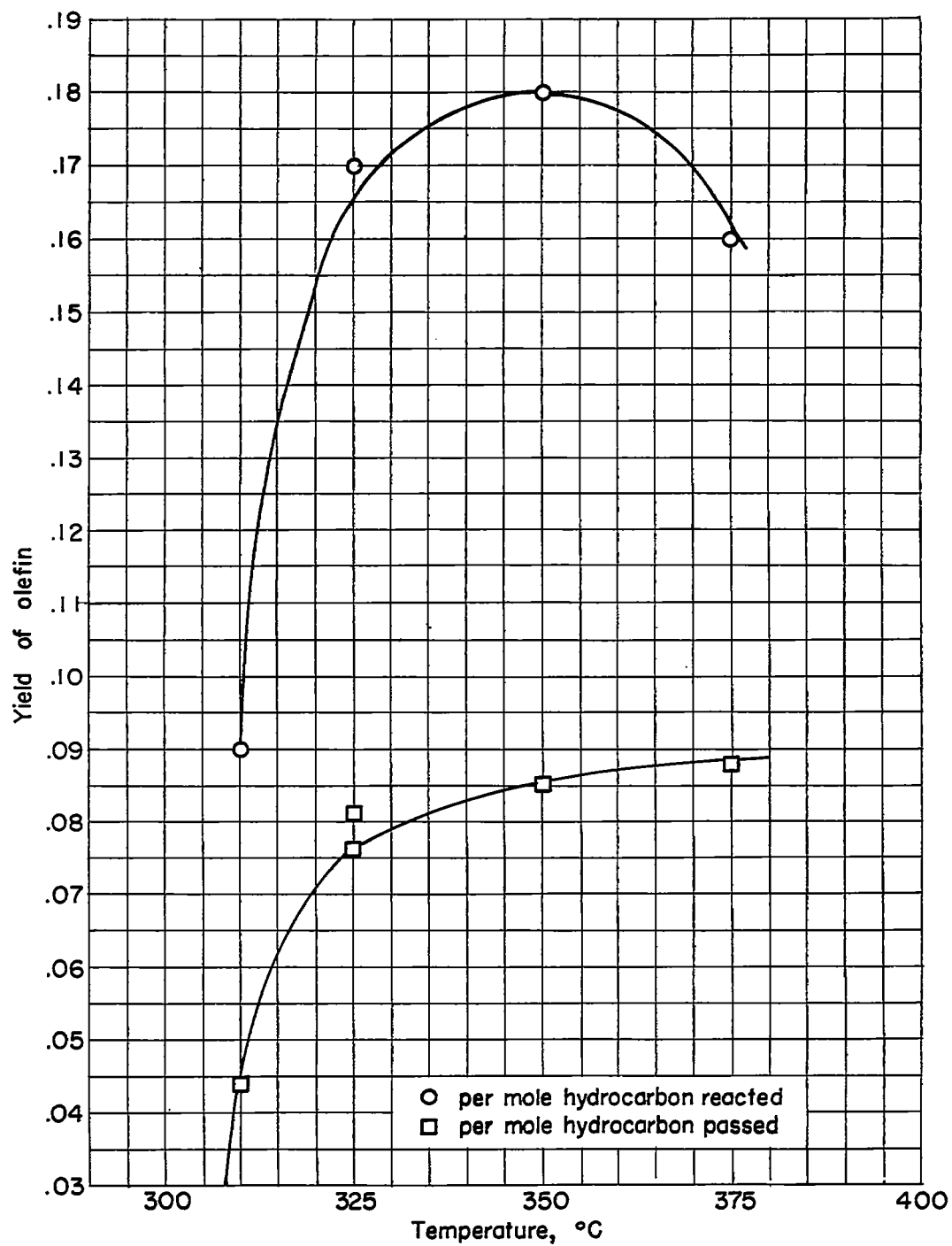
Figure 5.- Yield of olefin against temperature. Contact time,
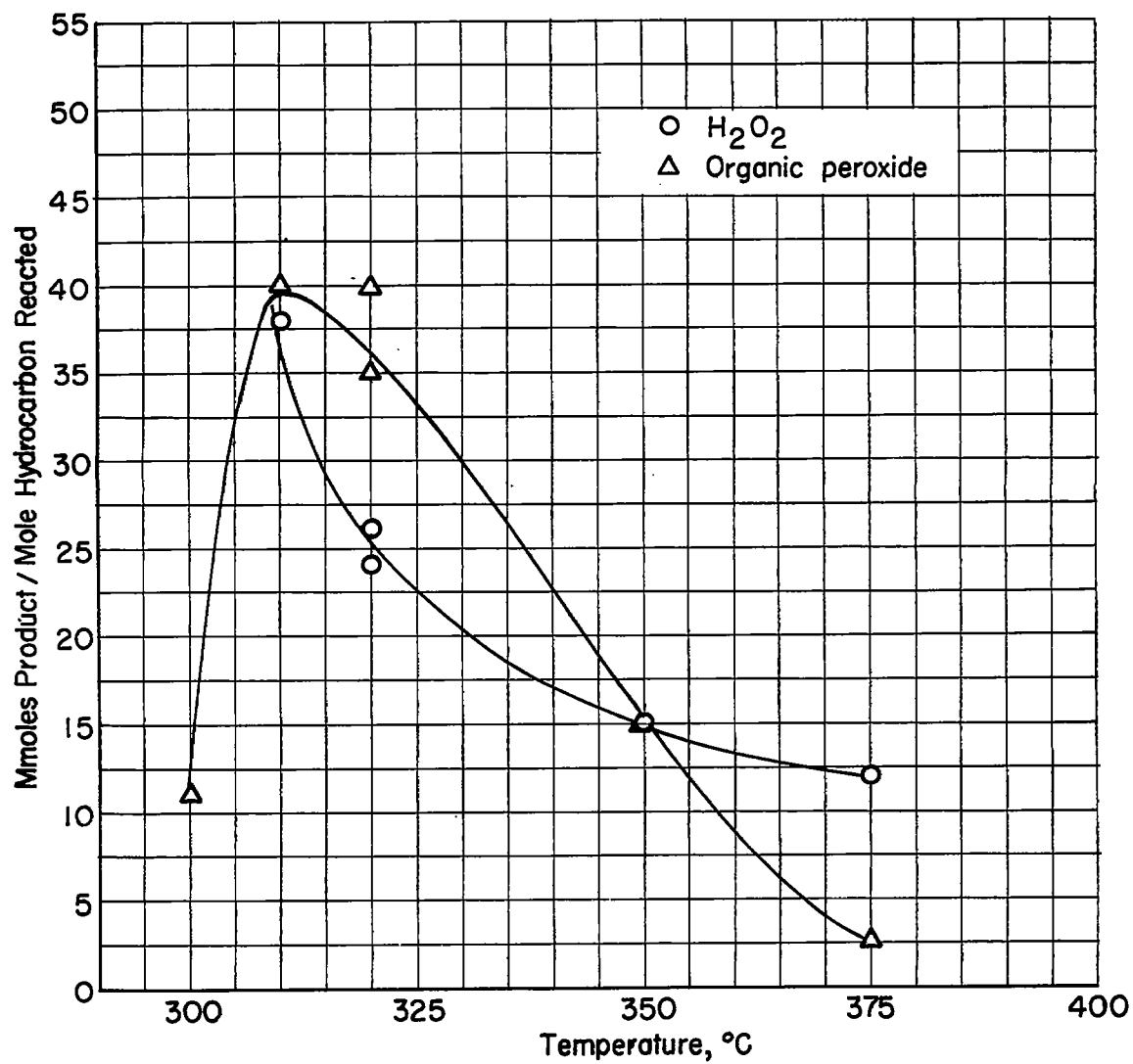8 seconds; stoichiometry, 0.1.

Figure 6.- Millimoles H_2O_2 and organic peroxide per mole methylcyclo-
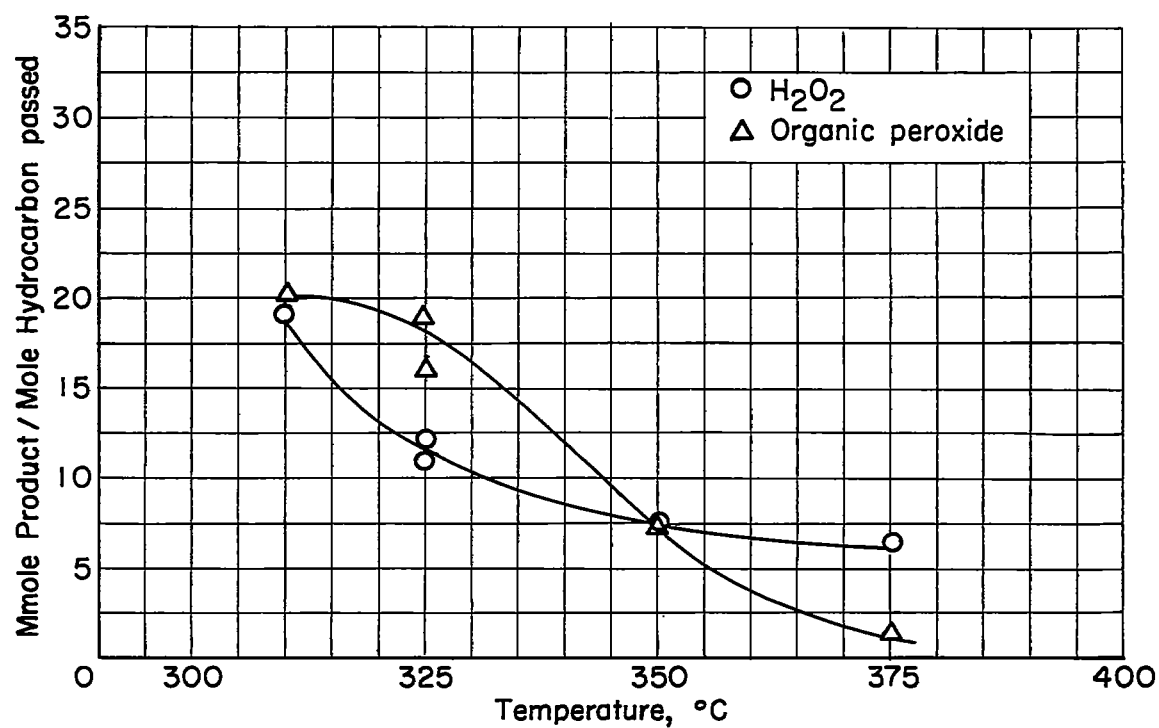hexane reacted against temperature. Contact time, 8 seconds;
stoichiometry, 0.1.

Figure 7.- Millimoles H_2O_2 and organic peroxide per mole methylcyclo-
hexane passed against temperature. Contact time, 8 seconds;
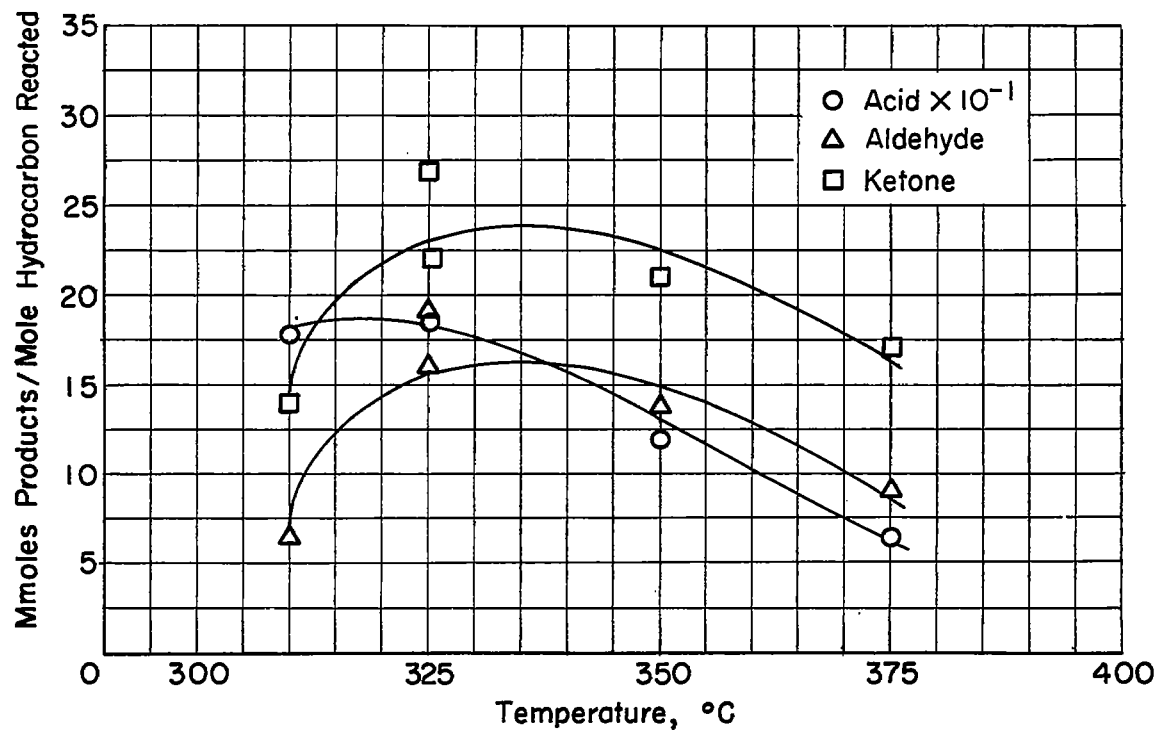stoichiometry, 0.1.

Figure 8.- Millimoles acid, aldehyde, and ketone per mole methylcyclo-
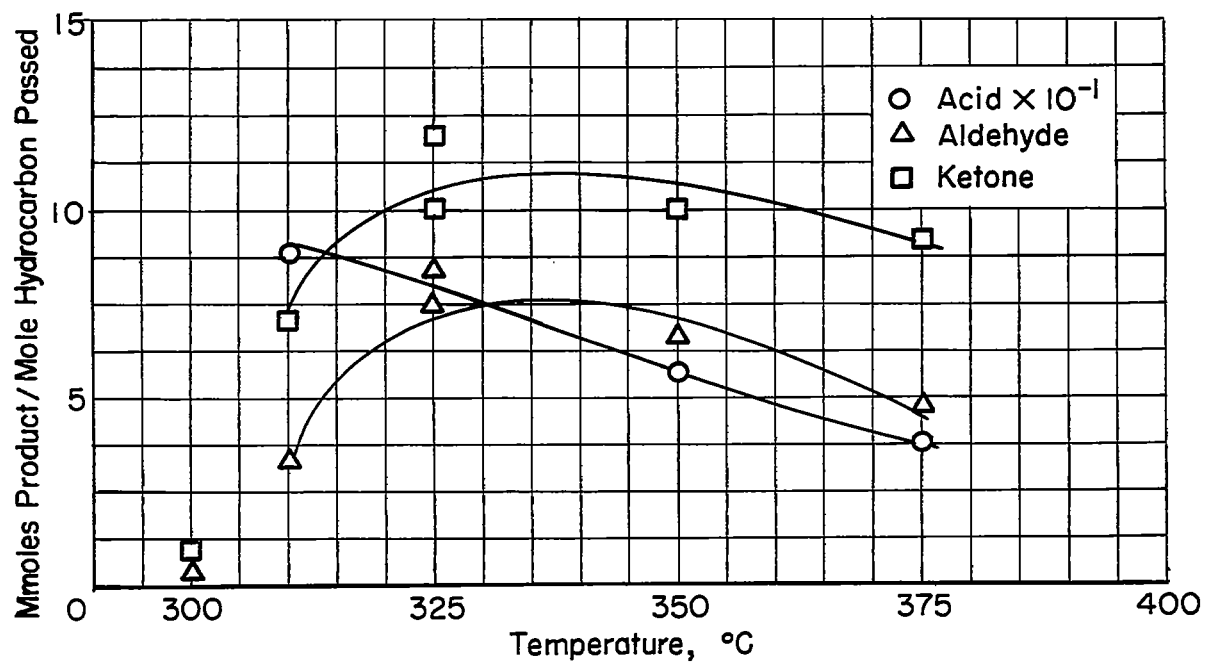hexane reacted against temperature. Contact time, 8 seconds;
stoichiometry, 0.1.

Figure 9.- Millimoles acid, aldehyde, and ketone per mole methylcyclo-
hexane passed against temperature. Contact time, 8 seconds;
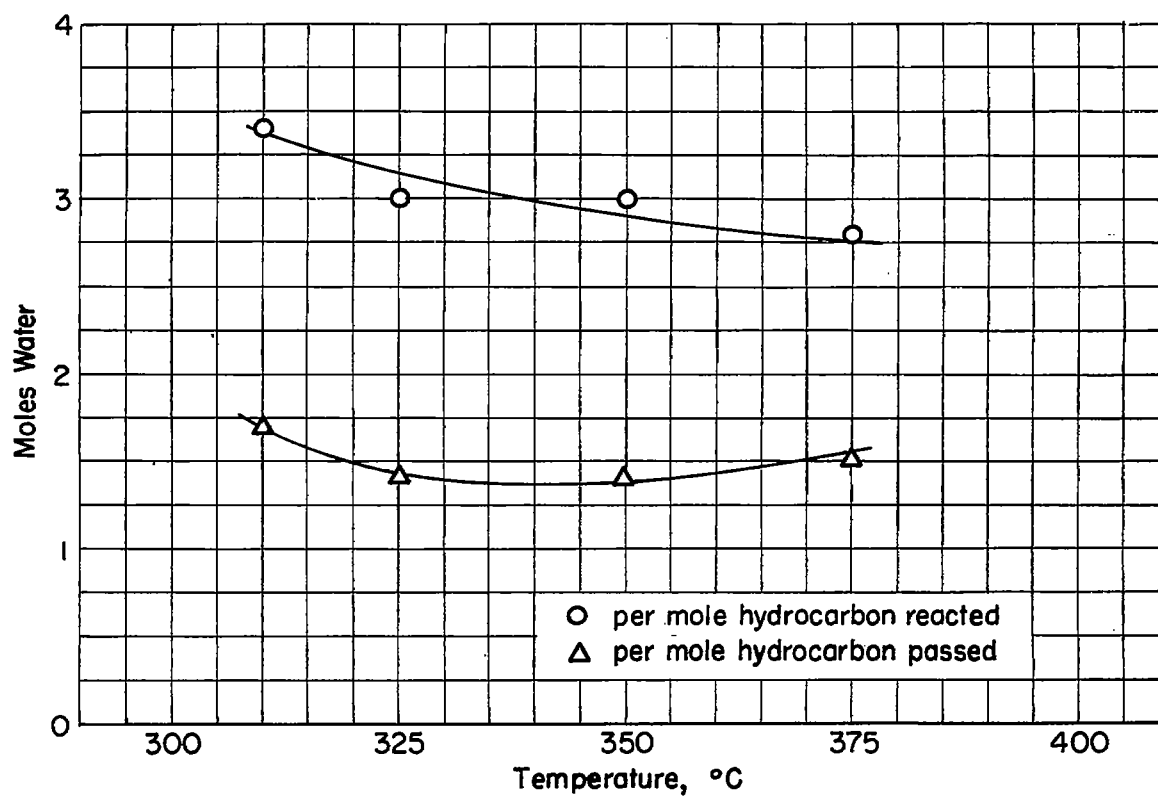stoichiometry, 0.1.

Figure 10.- Yield of water against temperature.   Contact time,
8 seconds; stoichiometry, 0.1.